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Synthesis of donor–acceptor conjugated polymers based on benzo[1,2-b:4,5-b′]dithiophene and 2,1,3-benzothiadiazole *via* direct arylation polycondensation: towards efficient C–H activation in nonpolar solvents†

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This article describes the synthesis of donor–acceptor (D–A) type copolymers based on benzo[1,2-b:4,5-b′]-dithiophene and 2,1,3-benzothiadiazole *via* direct-arylation cross-coupling polycondensation. To achieve high performance polymerization, we have systematically investigated the reaction factors including catalysts, solvents, ligands, bases, additives, concentration of reactants and phase transfer agents. In particular, 1,2-dimethylbenzene (ODMB), as a nonpolar high boiling point solvent, is a superior medium to perform this direct-arylation polymerization. In this nonpolar aromatic solvent, Pd$_2$dba$_3$/(o-MeOPh)$_3$P, accompanied with a base potassium carbonate and an additive pivalic acid, serves as an efficient catalyst system to obtain high-quality polymers. Our optimized condition gave the polymer with a weight-average molecular weight (M_w) as high as 60 kg mol^{-1} in nearly quantitative yield and excellent C–H selectivity.

Introduction

Conjugated polymers (CPs), due to their excellent optical and electronic properties, have attracted tremendous interest in the past decades from both academic and industrial fields. The so-called D–A conjugated polymers containing alternating electron-rich and electron-deficient units are particularly attractive due to the facile tunability of electronic structures in their conjugated backbones and consequently optoelectronic properties of polymers.[1–6] To date, most of D–A conjugated polymers have been synthesized by classic Stille coupling polycondensation or Suzuki coupling polycondensation.[7–9] But these reactions show disadvantages such as the necessity of prefunctionalizing monomers (arylstannanes or arylboron derivatives) using flammable and nonstable butyllithium. Other issues, particularly for Stille coupling, include the difficulty of purifying arylstannane monomers and the formation of toxic byproducts. To synthesize conjugated polymers *via* an economically efficient, safe and environment-friendly approach, special attention has been paid to carbon–hydrogen (C–H) direct arylation cross-coupling reaction.[9–12]

The protocols of C–H direct arylation towards synthesis of conjugated polymers have usually been borrowed from what has been learned from the synthesis of small organic molecules for pharmaceutics.[13,14] For example, Fagnou *et al.* have explored an effective synthetic protocol, which involves palladium acetate (Pd(OAc)$_2$) as a catalyst, *N,N*-dimethylacetamide (DMAc) as a solvent, potassium carbonate (K$_2$CO$_3$) as a base and pivalic acid (PivOH) as an additive, for direct arylation of aromatic compounds.[15,16] This synthetic protocol has been successfully applied to the synthesis of many conjugated polymers.[17–29] The catalyst Pd(OAc)$_2$ is particularly efficient in highly polar solvents such as DMAc, in which most low polar or nonpolar conjugated polymers show limited solubility. Therefore, highly polar solvents are not ideal reaction media for synthesis of conjugated polymers, particularly for those decorated with hydrophobic alkyl side chains.

Very recently, there has been some progress in exploring low polar or nonpolar solvents as the reaction media for synthesis of conjugated polymers. For instance, Ozawa *et al.* have used tetrahydrofuran (THF) instead of highly polar solvents to synthesize poly(3-hexylthiophene-2,5-diyl) (P3HT), to ensure the solubility of the resulting polymers during polymerization.[30] Herrmann's catalyst (*trans*-Di-μ-acetatobis[2-[bis(2-methyl-phenyl)phosphine]benzyl]dipalladium), in the presence of an appropriate ligand, was proven to be an effective catalyst in this reaction system to afford high-molecular-weight P3HT with high regioregularity (98%), whereas the reaction catalyzed with Pd(OAc)$_2$ in the same solvent was not reproducible and

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frequently provided low molecular weight products. Later, Leclerc *et al.* have utilized this reaction condition with modifications to synthesize a series of D–A type conjugated polymers.[31–36] The reaction was typically performed with heating at 120 °C. The overheated solvent (THF) and the necessity of using a sealed and pressurized reaction container, however, may compromise the reproducibility of the polymerization and raise the cost as well as safety concerns for performing and scaling up the synthesis. In addition, some monomers cannot be polymerized in THF with Herrmann's catalyst.[36] More recently, Ozawa *et al.* have reported another efficient catalytic system based on tris(dibenzylideneacetone)dipalladium(0)-chloroform adducts (Pd$_2$(dba)$_3$·CHCl$_3$) for polycondensation of 2,7-dibromo-9,9-dioctylfluorene and 1,2,4,5-tetrafluorobenzene.[37] This catalytic system was sufficiently reactive in both THF and in toluene to afford the polyphenylene derivative with high molecular weight and high yield.

Despite these recent advances, little study has been carried out in exploring high boiling point nonpolar solvents for efficient synthesis of conjugated polymers *via* direct arylation polycondensation. Even less has been understood with reaction factors that affect the direct arylation polycondensation in nonpolar solvents.

In this article, we report such a direct arylation polycondensation system. Our target polymer, denoted as **PBDTBT**, consists of alternating benzo[1,2-*b*:4,5-*b'*]dithiophene (**BDT**) as an electron donor (D) and 2,1,3-benzothiadiazole (**BT**) as the electron acceptor (A). Both **BDT** and **BT** have been among the most popular building blocks in a variety of D–A conjugated polymer semiconductors.[1–6,38–47] Two long branched 2-hexyldecyloxy groups were introduced to the **BDT** segment to afford good solubility of **PBDTBT** in a variety of solvents.

To optimize the polymerization of **BDT** and **BT** under the scheme of direct arylation, we have systematically examined a broad range of factors, including a series of low polar or nonpolar solvents, catalysts, ligands, bases, additives, reactant concentrations and phase transfer agents. Our optimized condition for direct arylation gives high molecular weight **PBDTBT** in a nearly quantitative yield with good regioregularity.

Results and discussion

Scheme 1 shows the synthetic route to the polymer **PBDTBT** *via* palladium-catalyzed direct arylation coupling reaction between monomers 4,8-di(2-hexyldecyloxy)benzo[1,2-*b*:4,5-*b'*]-

dithiophene (**HDBDT**) and 4,7-dibromobenzothiadiazole (**BrBT**). The following sections describe our systematic study of the factors that influence this direct arylation polymerization.

Effect of catalysts

Palladium(0) (Pd(0)) usually serves as the major active species in most of palladium-catalyzed cross-coupling reactions. However, due to labile characteristics, the Pd(0) complexes usually need to be reduced *in situ* from palladium(II) (Pd(II)) complexes and manifolded with varying coordination shells to form reactive species.[48,49] So the chemical characteristics of palladium catalysts, also known as catalytic precursors, are important to determine their activity in a cross-coupling reaction. We examined activities of different palladium complexes for polymerizing **HDBDT** and **BrBT**. As shown in Table 1, the polymerization using Herrmann's catalyst in THF resulted in **PBDTBT** with a low number-average molecular weight (M_n) of 4.1 kg mol^{-1}, indicating that the activity of the Herrmann's catalyst is not sufficient to activate the C–H bonds at positions 2- and 6- of **BDT** to form high molecular weight polymers. As can be expected, **PBDTBT** prepared using Pd(OAc)$_2$ in DMAc precipitated from the reaction system in the process of polymerization and formed metallic luster polymer pellets. The solubility limitation of the resulting polymer in DMAc blocked further growth of polymer chains, especially for the molecules surrounded by others in the precipitated particles. As a result, using DMAc as the reaction medium gave the polymer **PBDTBT** with a relatively high polydispersity index (PDI) of 2.9. Compared with Pd(OAc)$_2$ in DMAc, the Pd$_2$dba$_3$ catalyst in THF led to similar weight-average molecular weight (M_w), but improved M_n with a relatively low PDI of 2.0.

To further compare the polymers prepared using these different catalytic systems, absorption spectra of the polymers were collected (Fig. 1). As expected, **PBDTBT** synthesized using Herrmann's catalyst/THF, due to its much lower molecular weight, shows an absorption peak at a shorter wavelength (545 nm) than the other two polymers synthesized using Pd(OAc)$_2$/DMAc (568 nm) and Pd$_2$dba$_3$/THF (638 nm), respectively. Surprisingly, the polymers synthesized using Pd(OAc)$_2$/DMAc and Pd$_2$dba$_3$/THF, respectively, despite their similar M_w, show much different optical absorption properties. The latter shows an absorption peak and the onset at longer wavelengths, corresponding to a longer average conjugation length. The average conjugation length of CPs is determined by maximum
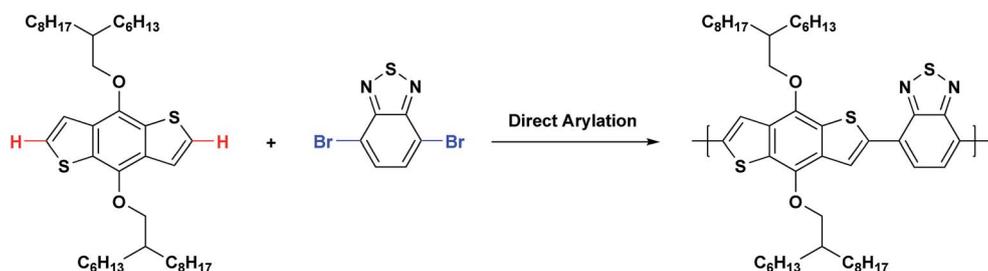
Scheme 1 Synthetic route to the polymer PBDTBT.

Table 1 Polymerization results of HDBDT and BrBT in different catalyst systems[a]

Entry	Catalyst	Ligand	Solvent	Base	Yield (%)	M_n (kg mol^{-1})	M_w (kg mol^{-1})	PDI
1	Pd(OAc)$_2$	PCy$_3$·HBF$_4$	DMAc	K$_2$CO$_3$	98	11.0	32.2	2.9
2	Herrmann's catalyst	(o-MeOPh)$_3$P	THF	Cs$_2$CO$_3$	88	4.1	9.8	2.4
3	Pd$_2$dba$_3$	(o-MeOPh)$_3$P	THF	Cs$_2$CO$_3$	99	16.0	32.8	2.0

[a] **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were polymerized in solvent (1 mL), in the presence of catalyst (5 mol%), ligand (10 mol%), base (0.6 mmol) and PivOH (0.06 mmol), at 100 °C for 24 h.
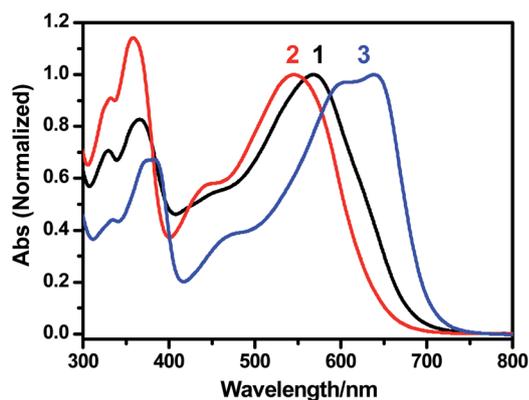

Fig. 1 Absorption spectra of chloroform solutions of **PBDTBTs** synthesized with different catalysts: line 1, 2, and 3 correspond to the polymers synthesized under the condition shown in entry 1, 2, and 3, respectively, in Table 1.

effective conjugation length, degree of polymerization (molecular weight) and structural defects.[4] Here, the difference of the conjugation length between **PBDTBTs** prepared with Pd(OAc)$_2$/DMAc and Pd$_2$dba$_3$/THF, respectively, might be mainly attributed to the structural defects, which is further discussed in the final section (Optical properties). The possible structural

defects in **PBDTBTs** prepared by direct arylation polymerizations are shown in Scheme 2.

To obtain more information about the molecular structures of **PBDTBTs** synthesized using Pd(OAc)$_2$/DMAc and Pd$_2$dba$_3$/THF, ^{1}H-NMR spectra of these polymers were collected. As highlighted with green rectangles in Fig. 2, marked regio-irregular sequence peaks at around 7.9 and 8.8 ppm are observed in the spectrum (line a) of **PBDTBT** synthesized using
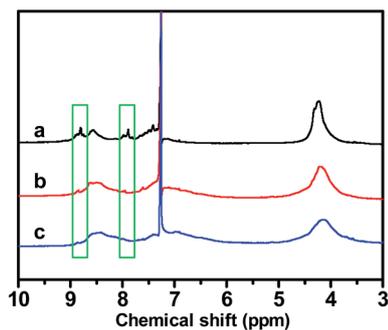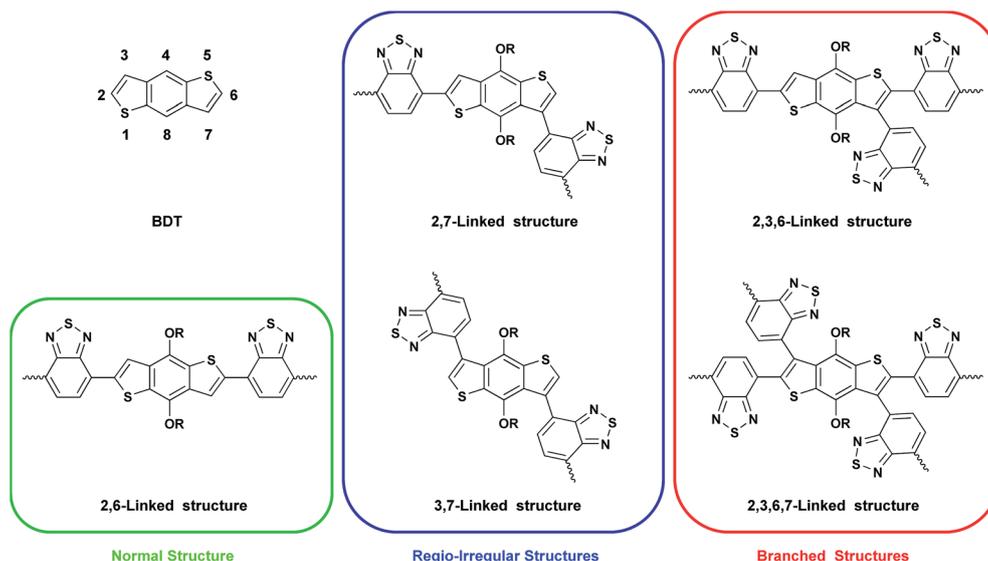

Fig. 2 ^{1}H-NMR spectra of **PBDTBTs** synthesized under different conditions: line a and b correspond to the polymers synthesized under the condition shown in entry 1 and 3 in Table 1; line c corresponds to the polymer synthesized under the optimized condition in ODMB (entry 1, Table 5).

Scheme 2 Possible structural defects in **PBDTBTs** prepared by direct arylation polymerizations.

Pd(OAc)$_2$/DMAc. These two peaks may be assigned to the protons of 6-unsubstituted benzo[1,2-*b*:4,5-*b*′]dithiophene and protons at 5 and 6 positions of benzothiodiazole which linked on the 3 and/or 7 positions of BDT, respectively, as shown in Scheme 2. In contrast, only negligible peaks exist in those regions for the polymer synthesized using Pd$_2$dba$_3$/THF (line b).

All the results described above indicate that Pd$_2$dba$_3$ is a superior catalyst in THF, compared to Herrmann's catalyst in the same solvent and Pd(OAc)$_2$ in DMAc for direct arylation polymerization of **HDBDT** and **BrBT**. Therefore, in the following sections, we focus on Pd$_2$dba$_3$ catalyst and discuss how other factors influence the direct arylation polymerization.
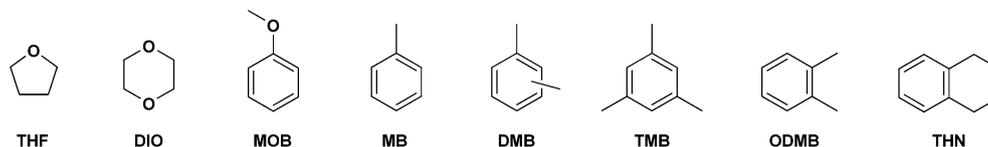
Effect of solvents

For most reactions involving C–H direct arylation coupling, transition-metal based catalysts, largely Pd(OAc)$_2$, show relatively higher reactivity in polar solvents than in nonpolar ones. Nevertheless, the influence of solvents on direct arylation still remains complex, as other factors also affect the polymerization result. To explore solvents appropriate for the Pd$_2$dba$_3$-catalyzed direct arylation polymerization, we systematically studied this polymerization in a variety of solvents, including THF, 1,4-dioxane (DIO), anisole (methoxybenzene, MOB), toluene (methylbenzene, MB), xylene (dimethylbenzene, DMB), mesitylene (1,3,5-trimethylbenzene, TMB), ODMB and tetrahydronaphthalene (THN). The chemical structures of the solvents used in the direct arylation polymerizations are summarized in Scheme 3. As shown in Table 2, the common low polar or nonpolar ether and arene solvents can serve as the reaction media for efficient Pd$_2$dba$_3$-catalyzed direct arylation. Interestingly, all the tested solvents give the polymers with a rather high yield (≥95%) but quite different molecular weights. Although

no clear relationship between polarity of the reaction solvent and molecular weight of the resulting polymers can be concluded from these experiments, the ether solvents with higher polarity than the arene solvents tend to give polymers with higher molecular weights. In addition, it appears that some extremely high boiling point solvents (*e.g.* TMB and THN) are unfavorable for the Pd$_2$dba$_3$-catalyzed polymerization.

It is worthwhile to note that, in ODMB, the polymerization gives a comparable result to that in THF, indicating that ODMB is a promising reaction medium for Pd$_2$dba$_3$-catalyzed coupling polymerization. As mentioned in Introduction, most of direct arylation polymerizations for the synthesis of conjugated polymers have been carried out in high-boiling-point, highly polar solvents such as DMAc, in which high-molecular-weight polymer products often show limited solubility. In contrast, ODMB described above is a nonpolar aromatic solvent with a boiling point of 144.4 °C. Based on the "like dissolves like" principle, ODMB should possess good solubility for aromatic compounds, particularly for nonpolar and low polar molecules. Therefore, ODMB should be favorable for synthesis of a broad range of conjugated polymers. In addition, the significantly higher boiling point of ODMB than that of THF allows polymerization to be readily performed under ambient pressure.

Effect of ligands

Tris(2-methoxyphenyl)phosphine ((*o*-MeOPh)$_3$P) served as an exceptionally effective ligand for Pd$_2$dba$_3$-catalyzed coupling copolymerization of **HDBDT** and **BrBT** in ODMB. There was no polymerization, however, when (*o*-MeOPh)$_3$P was absent or replaced with other ligands, such as triphenylphosphane (Ph$_3$P), tris(2-methylphenyl)phosphine ((*o*-Tol)$_3$P), and tri-*t*-butyl phosphine ((*t*-Bu)$_3$P). The coordinating ability of *ortho*-

Scheme 3 Chemical structures and abbreviations of solvents used in the direct arylation polymerization.

Table 2 Effect of solvents on the polymerization of HDBDT and BrBT^{a,b}

Entry	Solvent	Boiling point (°C)	Dielectric constant	Dipole moment (10^{-10} C m)	Yield (%)	M_n (kg mol^{-1})	M_w (kg mol^{-1})	PDI
1	THF	66	7.58	5.67	99	16.0	32.8	2.0
2	DIO	101.3	2.209	1.50	97	14.1	31.0	2.2
3	MOB	153.7	4.33	4.00	96	13.2	23.7	1.8
4	MB	110.6	2.24	1.23	99	13.6	24.3	1.8
5	DMB	137–140	—	—	96	11.3	22.5	2.0
6	TMB	164.7	2.279	0.23	95	6.8	11.9	1.7
7	ODMB	144.4	2.266	1.47	98	14.2	31.1	2.2
8	THN	207.6	2.733	1.33	95	5.2	8.2	1.6

^{a} The physical properties of the solvents were from ref. 50. ^{b} **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were polymerized in a solvent (1 mL), in the presence of Pd$_2$dba$_3$ (5 mol%), (*o*-MeOPh)$_3$P (10 mol%), Cs$_2$CO$_3$ (0.6 mmol) and PivOH (0.06 mmol), at 100 °C for 24 h.

methoxy groups may play a particularly important role in the high efficiency of (o-MeOPh)$_3$P in the polymerization.[37]

Effect of bases

The presence of a base is necessary in a transition metal catalyzed coupling reaction to promote the efficiency of catalysts and increase the yield of products. The role of a base is not only to abstract protons and neutralize acids introduced and/or produced in the reaction system, but also to activate catalysts and facilitate regeneration of the reactive species. The performance of bases in reactions is determined by many factors, including the intrinsic factors such as basicity, nucleophilicity, and steric hindrance, as well as the extrinsic factors such as solubility, ionization ability, aggregation state, and coordination ability.

The results of copolymerization of **HDBDT** and **BrBT** in the presence of different bases are summarized in Table 3. Carbonates were examined firstly, due to their wide use in previous direct arylation polymerizations. Among the tested carbonates, potassium carbonate (K$_2$CO$_3$) gave optimal results; cesium carbonate (Cs$_2$CO$_3$) showed an acceptable polymerization result; sodium carbonate (Na$_2$CO$_3$) was ineffective, only giving trace oligomer/polymer; calcium carbonate (CaCO$_3$) and barium carbonate (BaCO$_3$) did not give any oligomer/polymer at all after a brief purification procedure.

The performance of carbonates should be related to their basicity and solubility. Solubility of the carbonates, both in typical solvents[51,52] and water, follows an order of Cs$_2$CO$_3$ > K$_2$CO$_3$ > Na$_2$CO$_3$ > CaCO$_3$ ≈ BaCO$_3$. In a Pd-catalyzed cross-coupling reaction, it is important to maintain a reasonable concentration of basic anions in the reaction system.[53] We speculate that the concentration of carbonate from K$_2$CO$_3$ in ODMB at the polymerization temperature (i.e. 100 °C) should be at a favorable level, compared to other carbonates, for the direct arylation polymerization of **HDBDT** and **BrBT**.

As K$_2$CO$_3$ showed better performance than other metal carbonates in the direct arylation polymerization, we further tested potassium bases with other anions. The polymerization results are shown in Table 3. Potassium phosphate (K$_3$PO$_4$) is also an effective base, outranked only by K$_2$CO$_3$. Compared to K$_3$PO$_4$, potassium acetate (KOAc) gives polymer products with a lower reaction yield and a lower M_n, which may be caused by its weak alkaline and less effective coordination with reactive catalytic centers. When potassium tert-butoxide (t-BuOK) was added to the polymerization system, the reaction mixture turned to dark brown while being heated in an oil bath. This phenomenon suggested that some reagents were decomposed or some side reactions occurred in the presence of such a strong base.

Finally, organic bases such as triethylamine (TEA), diisopropylethylamine (DIPEA), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and triethylenediamine (TEDA) were tested in the copolymerization of **HDBDT** and **BrBT**. But none of them resulted in the formation of polymer products. The presence of organic bases may lead to debromination of dibromobenzothiadiazole as the main reaction[54] and consequently interferes with the polymerization.

As K$_2$CO$_3$ showed the best performance among all the bases tested above, we further optimized the equivalence of K$_2$CO$_3$ (entries 2, 13, 14 and 15, Table 3) in the reaction mixtures. With the increase of K$_2$CO$_3$ from 2 to 5 equivalents, the molecular weight of the resulting polymers increased gradually. Further increase of the amount of K$_2$CO$_3$ to 10 equivalents, the molecular weight of the resulting polymers cannot be further improved.

Effect of additives

Carboxylate additives play an important role in transition metal catalyzed direct arylation reactions. It has been proposed that C–H bond transformations assisted by carboxylates proceed via a mechanism in which metalation takes place via a concerted base-assisted deprotonation.[55] Fagnou et al. have proved that the pivalate anion is a key component in cleaving of a C–H bond by lowering the cleavage energy of the C–H bond and acting as a catalytic proton shuttle from an unactivated substrate to the stoichiometric carbonate base.[15] In addition, DIPEA as an alternative to carboxylates shows improved selectivity in some cases.[56]

Table 3 Effect of bases on the polymerization of HDBDT and BrBT[a]

Entry	Base	Yield (%)	M_n (kg mol^{-1})	M_w (kg mol^{-1})	PDI
1	Cs$_2$CO$_3$ (3 eq.)	98	14.2	31.1	2.2
2	K$_2$CO$_3$ (3 eq.)	98	19.5	46.5	2.4
3	Na$_2$CO$_3$ (3 eq.)	Trace	—	—	—
4	CaCO$_3$ (3 eq.)	0	—	—	—
5	BaCO$_3$ (3 eq.)	0	—	—	—
6	K$_3$PO$_4$ (3 eq.)	96	18.0	39.7	2.2
7	KOAc (3 eq.)	85	5.4	8.5	1.6
8	t-BuOK (3 eq.)	0	—	—	—
9	TEA (3 eq.)	0	—	—	—
10	DIPEA (3 eq.)	0	—	—	—
11	DBU (3 eq.)	0	—	—	—
12	TEDA (3 eq.)	0	—	—	—
13	K$_2$CO$_3$ (2 eq.)	97	18.6	42.8	2.3
14	K$_2$CO$_3$ (5 eq.)	98	22.0	54.4	2.5
15	K$_2$CO$_3$ (10 eq.)	97	20.2	47.3	2.3

[a] **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were polymerized in ODMB (1 mL), in the presence of Pd$_2$dba$_3$ (5 mol%), (o-MeOPh)$_3$P (10 mol%), base and PivOH (0.06 mmol), at 100 °C for 24 h.

Table 4 Effect of additives on the polymerization of HDBDT and BrBT[a]

Entry	Additive	Yield (%)	M_n (kg mol^{-1})	M_w (kg mol^{-1})	PDI
1	None	68	3.4	7.7	2.3
2	PivOH (0.3 eq.)	98	19.5	46.5	2.4
3	DIPEA (0.3 eq.)	0	—	—	—
4	PivOH (0.5 eq.)	98	21.9	53.6	2.4
5	PivOH (1 eq.)	97	21.1	51.0	2.4

[a] **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were polymerized in ODMB (1 mL), in the presence of Pd$_2$dba$_3$ (5 mol%), (o-MeOPh)$_3$P (10 mol%), K$_2$CO$_3$ (0.6 mmol) and additive, at 100 °C for 24 h.

The effect of additives on the Pd_2dba_3-catalyzed copolymerization of **HDBDT** and **BrBT** in ODMB is summarized in Table 4. Surprisingly, the Pd_2dba_3-catalyzed polymerization was quenched upon addition of DIPEA as an additive. The presence of DIPEA may result in debromination of bromide monomers and thus quenches the coupling reaction.[54] In contrast to DIPEA, the addition of PivOH to the reaction mixture promoted the coupling copolymerization. For example, the addition of 0.5 equivalent (*vs.* the monomer) PivOH resulted in a more than 6-fold increase of molecular weight of the formed polymer, compared to that of the polymer synthesized without PivOH. In addition, this increase of molecular weight was accompanied by an increase of the reaction yield from 68% to 98%. A further increase of the amount of PivOH up to 1 equivalent (*vs.* the monomer) did not lead to significant improvement of the polymerization (entry 5, Table 4).

Effect of reactant concentration

Under the optimized reaction condition (entry 1 in Table 5), after several hours of polymerization, the resulting polymers precipitated from the reaction mixture occasionally onto the inner surface of the reaction vessel, producing a metallic luster "conjugated polymer mirror" on the inner vessel surface. One possible reason for the early precipitation of polymer products during the reaction can be the very high concentration (>160 mg mL^{-1}) of the formed polymers in the reaction medium. The precipitation of polymers from the concentrated reaction medium may limit the formation of high molecular weight polymers. To resolve the issue of precipitation, we added an extra solvent, ODMB, to dilute the reaction mixture. The polymerization results at different concentrations are summarized in Table 5. Unfortunately, the dilution of the reaction mixture slowed down the polymerization significantly. Although the yield of the reaction was little affected upon dilution of the reaction mixture, the average molecular weight of the polymer products fell gradually with the decrease of the reactant concentration from 0.2 to 0.05 M.

Effect of phase transfer agents

As discussed above, pivalic acid has been proven to be one of the most effective additives to enhance the reactivity of C–H bonds. Thompson *et al.* have proposed that *in situ* generated carboxylate anions acted as a soluble organic base to promote the reaction.[9] From this point of view, it appears that increasing the solubility of an inorganic base (*e.g.* K_2CO_3) in a reaction system might benefit direct arylation cross-coupling. Phase transfer agents (PTAs) have been widely used in heterogeneous reactions to facilitate the migration of an inorganic base from an aqueous phase or a solid state into an organic phase where the reaction occurs. Here, we studied the effect of a series of PTAs, including 1,4,7,10,13,16-hexaoxacyclooctadecane (18-Crown-6), aliquat336, tetra-*n*-butylammoniumbromide (TBAB), tetra-*n*-butylammoniumfluoride (TBAF), and tetra-*n*-butylammonium hexafluorophosphate (TBAPF6) on the direct arylation polymerization in ODMB. The results (Table 6) appeared to be too scattered to reach a clear conclusion. While the addition of 18-Crown-6, TBAPF6 or distilled water gave polymers with relatively low molecular weights; quaternary ammonium salts associated with simple anions (*i.e.* halide ions, including chloride ion in Aliquat 336, bromide ion in TBAB and fluoride ion in TBAF, respectively) nearly quenched the polymerization. This effect might have been caused by these extra anions from PTAs (if any) and the inorganic base solubilized by PTAs, that may block the free coordination sites of low-ligated Pd(0) complexes, which is necessary for the turnover of the catalyst.[53] As a result, the reactions were slowed down or even quenched.

Optical properties

We further studied the optical properties of the polymers synthesized under different conditions of direct arylation polymerizations described above. The absorption spectra of some representative polymers with different molecular weights synthesized in ODMB are presented in Fig. 3. The **PBDTBT** synthesized using $Pd(OAc)_2$/DMAc is also included for comparison. Table 7 summarizes the optical data, including absorption peak wavelengths (λ_{abs}), onset-absorption wavelengths (λ_{onset}), and full width at half maximum absorption (FWHM) of the polymers.

As expected, for the polymers synthesized in ODMB, gradual bathochromic shifts of both the absorption peak and the onset of absorption were observed with the increase of the molecular weight, accompanied with a decrease of the FWHM. The **PBDTBT** prepared using $Pd(OAc)_2$/DMAc (line 1) showed a slight

Table 5 Effect of reactant concentrations on the polymerization of HDBDT and BrBT[a]

Entry	Concentration	Yield (%)	M_n (kg mol^{-1})	M_w (kg mol^{-1})	PDI
1	0.2 M	98	24.5	60.1	2.4
2	0.1 M	99	19.5	45.0	2.3
3	0.05 M	97	13.8	26.6	1.9

[a] **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were polymerized in ODMB (1, 2, or 4 mL), in the presence of Pd_2dba_3 (5 mol%), (*o*-MeOPh)$_3$P (10 mol%), K_2CO_3 (1 mmol) and PivOH (0.1 mmol), at 100 °C for 24 h.

Table 6 Effect of phase transfer agents on the polymerization of HDBDT and BrBT[a]

Entry	PTA	Yield (%)	M_n (kg mol^{-1})	M_w (kg mol^{-1})	PDI
1	None	99	19.5	45.0	2.3
2	18-Crown-6	96	10.2	16.7	1.6
3	Aliquat336	Trace	—	—	—
4	TBAB	Trace	—	—	—
5	TBAF	Trace	—	—	—
6	TBAPF6	99	16.8	35.9	2.1
7	Water (0.4 mL)	99	9.2	15.7	1.7

[a] **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were polymerized in ODMB (2 mL), in the presence of Pd_2dba_3 (5 mol%), (*o*-MeOPh)$_3$P (10 mol%), K_2CO_3 (1 mmol), PivOH (0.1 mmol) and PTA (0.06 mmol), at 100 °C for 24 h.
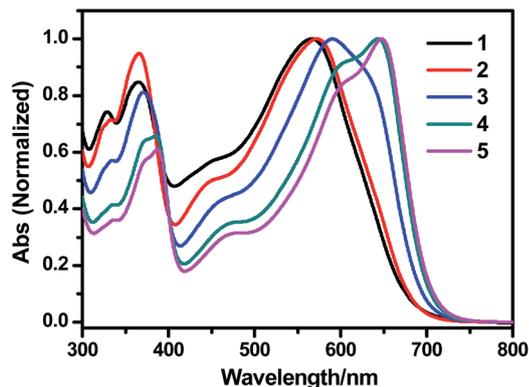
Fig. 3 Absorption spectra of chloroform solutions of PBDTBTs synthesized under different conditions: lines 1–5 correspond to the polymers entry 1–5 listed in Table 7 with the same sequence.

hypsochromic shift in its absorption spectrum, compared with the PBDTBT synthesized using Pd₂dba₃/ODMB and with a much lower molecular weight (line 2). In other words, the conjugation length of PBDTBT prepared using Pd(OAc)₂/DMAc with an M_n/M_w of 11.0/32.2 kg mol^{-1}, was even inferior to that of PBDTBT polymerized in ODMB with an M_n/M_w of 5.4/8.5 kg mol^{-1}. These results imply that some structural defects, presumably caused by the relatively poor regioselectivity in the polymerization, may exist in the polymer prepared using Pd(OAc)₂/DMAc.[9,11,22,23,27]

To further probe the structure of the polymers synthesized in ODMB, ^{1}H-NMR spectrum of a representative PBDTBT prepared under the optimized reaction condition (entry 1 in Table 5) was collected and the result is presented in Fig. 2 for comparison. A close inspection of the NMR spectrum reveals only slight distortion without any distinguishable peaks in the regions around 8.8 and 7.9 ppm. This result further suggests that the relatively poor C–H regioselectivity observed in Pd(OAc)₂-catalyzed polymerization in DMAc was suppressed in the Pd₂dba₃-catalyzed polymerization in ODMB.

In addition, the PBDTBTs that we synthesized here *via* direct arylation polymerization in ODMB (line 3 and 4) shows similar or even red-shifted absorption compared with the same type of polymer with a similar M_n but synthesized *via* Stille coupling by other research groups.[40,41] Again, these results suggest the good regioregularity of the polymers synthesized *via* Pd₂dba₃-catalyzed direct arylation polymerization in ODMB.

Conclusions

D–A type conjugated polymers based on BDT and BT have been synthesized by direct-arylation polycondensation. We have systematically investigated the reaction parameters, including catalysts, ligands, solvents, bases, additives and concentrations, and studied how each factor influences the direct arylation polycondensation. ODMB as a nonpolar and high-boiling-point solvent is a promising reaction medium to perform the direct-arylation polymerization. An optimized condition for reacting 0.2 M of HDBDT and stoichiometric BrBT with 5 mol% of Pd₂dba₃, 10 mol% of (o-MeOPh)₃P, 5 equivalents of K₂CO₃, 0.5 equivalents of PivOH in ODMB gives PBDTBT with a weight-average molecular weight of 60 kg mol^{-1} in almost quantitative yields and good regioselectivity. We expect that the knowledge that we gain from this system of direct arylation polymerization will be useful for economically efficient and environmentally-green synthesis of a broad scope of conjugated polymers for applications in optoelectronic devices, sensing and bioimaging.

Experimental section

Materials

HDBDT was synthesized according to the procedure described in a previous report.[44] BrBT and other reagents, solvents were of commercial grade and used as received without further purification. All reactions were performed under a nitrogen atmosphere.

Measurements and characterization

The number-average molecular weights (M_n), weight-average molecular weights (M_w) and polydispersity index (PDI, M_w/M_n) of the polymers were measured by gel permeation chromatography (GPC) using an Agilent 1260 Infinity system at 30 °C, with polystyrenes as reference standard and THF as an eluent. All new compounds were characterized by nuclear magnetic resonance spectroscopy (NMR). The NMR spectra were recorded on a Bruker AV 300 spectrometer at room temperature. UV-vis absorption spectra were recorded on a Shimadzu spectrometer

Table 7 Optical properties of PBDTBTs synthesized under different polymerization conditions

Entry	M_n/M_w (kg mol^{-1})	Polymerization condition	λ_{abs} in CHCl₃ (nm)	λ_{onset} in CHCl₃ (nm)	FWHM (nm)
1	11.0/32.2	Pd(OAc)₂/DMAc[a]	329, 365, 567	678	210
2	5.4/8.5	Pd₂(dba)₃/ODMB[b]	333, 366, 572	685	185
3	9.2/15.7	Pd₂(dba)₃/ODMB[c]	334, 370, 590	691	163
4	16.8/35.9	Pd₂(dba)₃/ODMB[d]	336, 385, 643	699	139
5	24.5/60.1	Pd₂(dba)₃/ODMB[e]	337, 387, 648	702	128

[a] Details of the polymerizations: DMAc (1 mL), Pd(OAc)₂ (5 mol%), PCy₃·HBF₄ (10 mol%), K₂CO₃ (0.6 mmol), and PivOH (0.06 mmol). [b] ODMB (1 mL), Pd₂dba₃ (5 mol%), (o-MeOPh)₃P (10 mol%), KOAc (0.6 mmol) and PivOH (0.06 mmol). [c] ODMB (2 mL), Pd₂dba₃ (5 mol%), (o-MeOPh)₃P (10 mol%), K₂CO₃ (1 mmol), PivOH (0.1 mmol) and water (0.4 mL). [d] ODMB (2 mL), Pd₂dba₃ (5 mol%), (o-MeOPh)₃P (10 mol%), K₂CO₃ (1 mmol), PivOH (0.1 mmol) and TBAPF6 (0.06 mmol). [e] ODMB (1 mL), Pd₂dba₃ (5 mol%), (o-MeOPh)₃P (10 mol%), K₂CO₃ (1 mmol) and PivOH (0.1 mmol). All these polymerizations were carried out with HDBDT (0.2 mmol) and BrBT (0.2 mmol) at 100 °C for 24 h.

model UV-2450. Absorption spectra measurements of the polymer solutions were carried out in chloroform at room temperature.

General procedures of polymerization

In a glove box, **HDBDT** (0.2 mmol), **BrBT** (0.2 mmol), catalyst (10 μmol), ligand (20 μmol), base, additive(s) and solvent were added in a reaction vial with a magnetic stirring bar. The vial was sealed with a rubber cap and then removed from the glove box. The vial was heated in a 100 °C oil bath for 24 hours. After being cooled to room temperature, the reaction mixture was diluted with 30 mL of chloroform and then filtered to remove the insoluble species. The filtrate was concentrated and added dropwise to 100 mL of ethanol, filtered through a Soxhlet thimble, and then subjected to Soxhlet extraction with methanol and chloroform sequentially. The chloroform fraction was concentrated and precipitated in 100 mL of ethanol. The precipitates were collected by filtration and dried under vacuum for one day to yield the target polymer

When purifying the reaction mixtures from different batches of polymerizations, we tried to remove unreacted starting materials and low molecular weight organic and inorganic impurities and collect all the resulting polymers and oligomers present in final products in order to completely compare the polymerizations under different reaction conditions.

Acknowledgements

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